

Effect of the oxygen reduction catalyst loading method on the performance of air breathable cathodes for microbial fuel cells

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Abstract This paper presents three different methods of hydrothermal (HT), microwave (MW), and cyclic voltammetry (CV) used to load a catalyst on a cathode surface. In the HT and MW methods, a multiwall carbon nanotube (MWCNT) is used as a support material to fix the catalyst, while Nafion solution is used as a binder to load the catalyst on the cathode surface. For the third option, the CV method is used to directly load the catalysts on the cathode surface without any support material. The performances of the three cathodes are tested in an air breathable batch microbial fuel cell (MFC) and compared to that of a commercial carbon cloth cathode with platinum (Pt). The maximum power density of the MFC with the HT cathode is measured as 833 mW m^{-2} , which is higher than those of the CV and MW cathodes and slightly smaller than the MFC with the Pt cathode. The open circuit voltage of the

MFC with the HT cathode is 610 mV, which is higher than those of MFCs with other cathodes, while the power density is higher than the MFCs of the MW and CV cathodes. In the case of the HT cathode, a conductive MWCNT network is well formed and entangled with the catalyst nanostructure of the cathode surface while the small ohmic and activation resistances of the HT cathode contribute to the good MFC performance.

Keywords Microbial fuel cell · Oxygen reduction · Catalyst loading · Hydrothermal

1 Introduction

The interesting anaerobic technology of microbial fuel cell (MFC) is used to convert chemical energy contained in organic matter into electricity [1, 2]. Aerobic biological treatment based on activated sludge has typically been used for wastewater treatment. However, the aerobic biological process is energy consuming and expensive due to the aeration required to maintain the dissolved oxygen during wastewater treatment and to treat and dispose the excess sludge [1–4]. In contrast, MFC collects electrical energy as a by-product during wastewater treatment [2, 4]. Because organic matter is degraded under anaerobic conditions in an MFC, the aeration facility needed to supply oxygen into the wastewater is eliminated in an MFC, and the excess sludge production is smaller than that found in the aerobic biological process [1–3, 5].

An MFC consists mainly of an anode and a cathode that are separated by a separator. The organic matter is degraded by the electrochemically active bacteria growing on the anode surface, and produce electrons and protons. The electron is transferred to the anode and then moves through

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an external circuit to the cathode. The proton moves to the cathode through the electrolyte and the separator. The electron and the proton on the cathode combine with oxygen as an electron acceptor to form water. Electrical power is collected via an external load installed in the circuit. One of the important factors affecting MFC performance is the oxygen reduction efficiency of the cathode [1, 3, 5]. The cathode's efficiency of oxygen reduction depends on the electrical conductivity and specific surface area of the cathode material, and the catalyst for oxygen reduction [3, 5]. A good choice of a cathode material is a carbon nanotube (CNT) with a specific surface area of $254\text{--}449\text{ m}^2\text{ g}^{-1}$, and the conductivity of $500\text{--}10^4\text{ S m}^{-1}$ [6, 7]. The catalyst of oxygen reduction plays an important role in lowering the activation energy of the oxygen reduction reaction [1, 3, 5]. It is well known that Pt is the best catalyst for oxygen reduction, but the high cost of Pt limits its use for practical wastewater treatment [1, 4, 5]. Several studies have recently been conducted to find a replacement catalyst for Pt, and the oxygen reduction efficiency of some transient metal compounds including CoTMPP, FePC, MnOx, and CuPC have been shown as similar to that of Pt [4, 8–13]. The oxygen reduction catalyst is generally loaded on the cathode surface using different methods such as CV, pyrolysis, hydrothermal (HT), and MW methods. The method used is important because the oxygen reduction efficiency is significantly affected by the loading method [13–17].

This study uses three different loading methods (HT, MW, and CV) to form a catalyst layer containing metal catalysts on the surface of cathodes. The performances of the methods in an MFC are then examined and compared to that of a commercial carbon cloth cathode using Pt as an oxygen reduction catalyst in an MFC.

2 Materials and methods

2.1 Electrodes preparation

The basic material for a primitive electrode is a pristine MWCNT (Carbon Nano-material Technology Co., Ltd., Pohang, Korea). In addition to this, a stainless steel mesh (#30, STS 316L) was purchased from a local hardware store. The MWCNT is immersed in nitric acid for 24 h to remove impurities, washed with running tap water to neutralize it, and dried in a drying oven. The prepared MWCNT (70 % dry wt.) is mixed with a polytetrafluoroethylene (PTFE) solution (60 % dry wt. PTFE dispersed in water, Sigma-Aldrich Co., St. Louis, USA) as a hydrophobic binder, and the mixture (0.04 g) of MWCNT and PTFE is screen-printed on the SS mesh ($4 \times 4\text{ cm}^2$) to form a hydrophobic layer. A primitive MWCNT electrode

is prepared by three times brushing of the PTFE solution onto the surface of the hydrophobic MWCNT three times layer and then hot-pressing at $370\text{ }^\circ\text{C}$ for 20 min to form a waterproof and air breathable layer. The cathodes are completed by loading a metal catalyst mixture for oxygen reduction by the three methods under examination. A commercial carbon cloth with Pt (5.0 g m^{-2} , GDE LT250EW, E-Teck) is used as the control cathode. For the anode, graphite fiber fabric (GFF, Samjung C&G Co., Korea) is fixed to the SS mesh (#30, STS 316L, $4 \times 4\text{ cm}^2$) via sewing with nylon thread.

2.2 Preparation of oxygen reduction catalyst on the primitive electrode

The oxygen reduction catalyst is a multi-metal complex (Fe–Cu–Mn), and the three cathode types are prepared by loading the catalyst complex on the hydrophilic surface of the primitive electrode with HT, MW, and CV. Briefly, the HT method uses high vapor pressure and temperature to activate the catalytic activity.

A multi-metal solution is prepared by dissolving sodium dodecyl sulfate 12.5 g, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$ 30.125 g, KMnO_4 19.75 g, FePc 0.5684 g, CuPc 0.5761 g, and MWCNT 1.875 g in 1.0 L of distilled water. To obtain a catalyst mixture consisting of MWCNT and the multi-metals (Fe–Cu–Mn), this solution is autoclaved at $135\text{ }^\circ\text{C}$ for 4.5 h, washed three times with ethanol solution, and centrifuged at 2,000 rpm for 10 min. For the MW method, the multi-metal solution is prepared similar to the HT method, except that the solution is heated five times using intermittent microwave radiation (1.5 min on for heating and 1.0 min off for cooling) instead of autoclaving. The mixture of the multi-metal catalyst is then prepared using the HT method. The prepared multi-metal catalysts (3 g) are mixed with a solution of ethanol (300 mL) and Nafion (30 % wt., 6.72 mL) as a binder to form the catalyst inks. The catalyst inks prepared using the HT and MW methods are screen-printed on the hydrophilic surface of the primitive electrode, and the catalyst is loaded on the electrode at 0.37 g cm^{-2} .

The CV method electrochemically fixes the catalyst on the primitive electrode. An electrolyte containing a multi-metal solution for the CV is prepared by dissolving FePC 0.5684 g, CuPC 0.5761 g, H_2SO_4 28 mL, and aniline 9.11 mL in 1.0 L of distilled water. The MWCNT is not used as basic materials in CV method, because the mixture of MWCNT and metal catalysts does not form substantial layer on the surface of the primitive electrode. The primitive electrode is dipped in the electrolyte solution and then subjected to 1.2 V for 100 min using a potentiostat (Ivium Tech., The Netherlands) to combine the FePC and CuPC on its the surface. This is then used as the working electrode, a Pt mesh ($2 \times 2\text{ cm}^2$) is used as the counter, and the

Ag/AgCl electrode is used as the reference electrode. Another electrolyte is then prepared by dissolving $\text{Mn}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ 24.5 g and NaSO_4 14.2 g in 1.0 L of distilled water, and CV is performed 600 times between 0.1 and 0.6 V to affix the MnOx onto the hydrophilic surface of the primitive electrode.

2.3 MFC reactor and its operation

This study uses a cube-type batch MFC reactor the effective anode volume of which is 972 mL ($9 \times 9 \times 12 \text{ cm}^3$). The four different cathodes prepared by the HT, MW, CV, and control (carbon cloth with Pt) methods are installed in each vertical hole of four walls. An anode is fitted on the inside of each cathode together with a non-woven polypropylene sheet as a separator. To form an external circuit, the anode and the cathode are connected using a copper wire, and an external resistance (200 Ω) is inserted in the circuit. To begin, anaerobic sewage sludge taken from the S sewage treatment plant (B metro-city) is screened and seeded into the anodic chamber (30 % volume). Synthetic wastewater containing acetate (1.000 mg L^{-1}), phosphate buffer solution (50 mM), minerals (12.5 mL L^{-1}), vitamins (5 mL L^{-1}), are prepared according to guidelines laid down by Wang et al [16]. The MFC reactor was mixed with a magnetic bar in a temperature-controlled room (30 $^\circ\text{C}$). During the operation, the voltage is monitored at 30 min intervals using a digital multimeter (DMM, Keithley 2700) connected to a personal computer, and the wastewater is replaced with fresh synthetic wastewater when the voltage reaches a level below 20 mV.

2.4 Analysis and calculation

Electrochemical analyses of the four cathodes prepared by different methods are performed via CV using a potentiostat with a three-electrode system. The cathode is the working electrode, while Ag/AgCl and Pt mesh are the reference and counter electrodes, respectively. The electrolyte is prepared by dissolving potassium hexacyanoferrate (III) 0.329 g and potassium nitrate 50.5 g into 1.0 L of distilled water. CV is taken between -0.2 and 1.2 V at 100 mV s^{-1} . Removing the background to produce on flat baseline of the CV curve allows identification of the peak currents and voltages. The surface morphology of the cathodes is obtained using scanning electron microscopy (SEM, JEM-1010, Hitachi Ltd., Japan) images. During MFC operation, the system is considered stable when the voltage change trends are similar over three cycles. In the steady state, the circuit is opened to obtain the open circuit voltage (OCV), and voltage change is monitored according to manual step decreases of the external resistance from 1,000 to 1Ω to obtain the polarization curve. The current is

calculating by dividing the voltage by the external resistance, while the power density (P_d , mW m^{-2}) was obtained by the product of the current density (I_d , mA m^{-2}) based on the cathode area and the voltage.

3 Results and discussion

3.1 Characterization of cathodes by catalyst binding methods

SEM images of the surfaces of the three cathodes prepared using the HT, MW, and CV methods are shown in Fig. 1. The cathode surfaces display different morphologies (Fig. 1a). Interestingly, a dense rod type network of MWCNT that is entangled with the catalyst nanostructure appears on the catalyst layer of the HT. It is possible that the MWCNT network has a positive influence on the electric conductivity of the catalyst layer of the cathode surface [14]. One of the major constituents of the internal resistance of an MFC is the ohmic resistance of the electrode [1, 3, 5].

In the case of the MW method, the MWCNT network also appears on the nanostructure catalyst layer, but it is a little sparse, compared to that of the HT (Fig. 1b). A coc-cus-type nanostructure appears on the catalyst layer of the CV, but the MWCNT network does not. This is because the catalyst of the CV is directly fixed to the surface of the primitive electrode by the electrochemical technique instead of the MWCNT support for the metal catalyst.

To compare the electrocatalytic reduction activity of the four cathodes (HT, MW, CV, and Pt), CVs for the cathodes are taken in a potassium hexacyanoferrate (III) solution. Both a positive shift of the reduction potential and an increase in the current indicate enhanced cathodic reduction activity [18]. The reduction current peaks of the four cathodes are obtained by removing the background to produce on flat baseline method from each CV curve (Fig. 2). The peak potential for the HT is 490 mV versus Ag/AgCl, which was lower than 650 mV of the Pt (Table 1). In the case of oxygen reduction reaction, the two electron reaction forming hydrogen peroxide is the main route to dispose electrons if the reduction potential is low [19, 20]. However, the peak current (9.95 mA) for the HT was much higher than that of the Pt (1.32 mA), indicating that the rate of the reduction reaction is quite high. It is possible that the HT is an excellent cathode catalyzing the cathodic reduction reaction. The peak potentials for the MW and the CV are 730 and 700 mV, respectively, which are quite high compared to the Pt. However, their peak currents (0.73 mA for the MW and 1.06 mA for the CV) are smaller than that of the Pt (Table 1). The reduction reactions of the MW and the CV are believed to be hindered by some internal resistances.

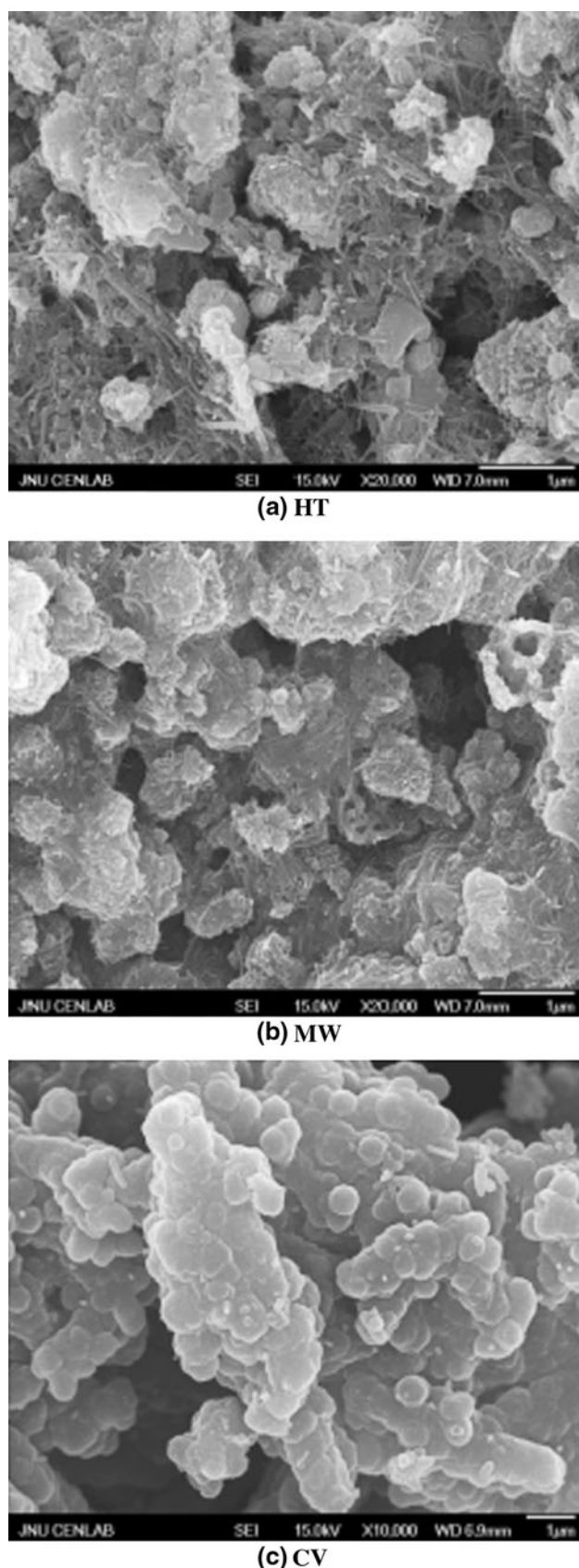


Fig. 1 Scanning electron microscopy images of the cathode surfaces prepared by the HT (a), MW (b), and CV (c) methods

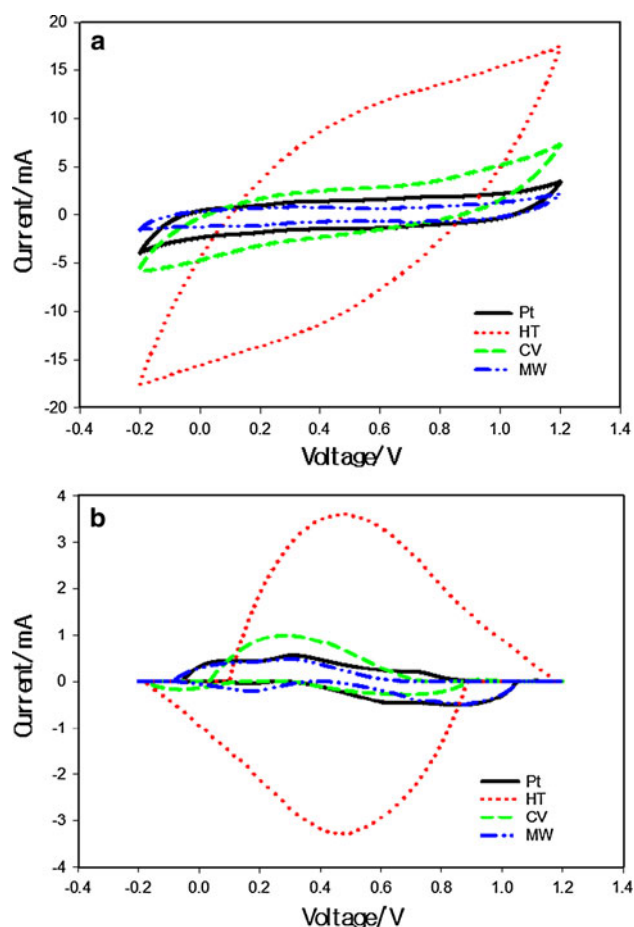


Fig. 2 Cyclic voltammograms of Pt, HT, CV and MW at a scan rate of 100 mV s^{-1} **a** after removing the background to produce on flat baseline **b** in 1 mM potassium hexacyanoferrate (III) dissolved in 0.5 M potassium nitrate

Table 1 Reduction peak voltages and currents of the cyclic voltammograms for the HT, MW, CV, and Pt cathodes

Cathode	Reduction peak voltage (mV)	Peak current (mA)
HT	490	9.95
MW	730	0.73
CV	700	1.06
Pt	650	1.32

HT hydrothermal, MW microwave, CV cyclic voltammetry, Pt platinum

3.2 Performance of the MFC with different cathode catalyst loading methods

The voltage increase trends of the MFCs during the initial acclimation period do not vary much across the types of cathodes. The voltages of the MFCs with four different cathodes (HT, MW, CV, and Pt) begin to increase 1 day after the start-up and are seen to increase rapidly from 1 to

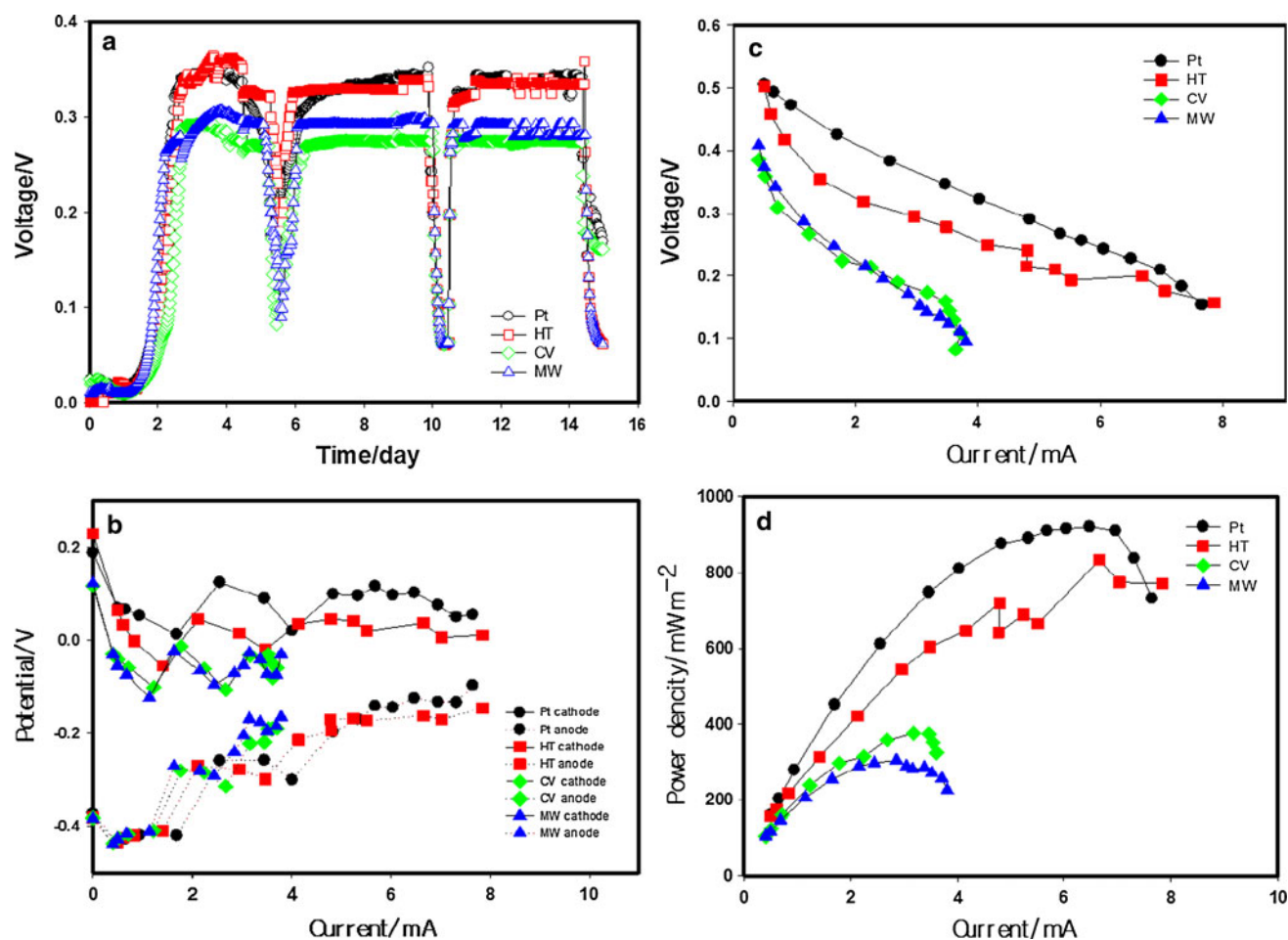


Fig. 3 Trends of voltage changes with time (a), voltages with current for the anodes and cathodes (b) and for the whole system (c) and power curve (d) for the MFCs with the cathodes according to catalyst loading method

3 days (Fig. 3a). The voltages approached the maximum values at around 3 days and then quickly dropped due to substrate depletion. The maximum voltages are fairly dependent on cathode type and can be listed in the order of HT > Pt > MW > CV in the first cycle. The electrolyte in the anode chamber is replaced with fresh electrolyte when the voltage drops to <20 mV. In the second cycles, the stable voltages of the MFCs with four cathodes are 340, 335, 275, and 292 mV for the Pt, HT, CV, and MW, respectively. The stable voltages of the third cycle are similar to those in the second cycle. The OCVs of the MFCs with four cathodes are measured by opening the circuits at stable voltages to obtain polarization curves (Fig. 3b). The anode potentials of the MFCs with four cathodes are similar on the I–V curve, but the cathode potentials with the current are obviously different according to cathode type (Fig. 3c). This indicates that the MFC performance estimated from the polarization curve is significantly affected by the cathode oxygen reduction efficiency. The maximum power density of the MFC with the

HT cathode is 833 mW m^{-2} , which is higher than that of MW (304 mW m^{-2}) and CV (376 mW m^{-2}), and slightly smaller than that of Pt (920 mW m^{-2}).

In order to investigate the causes of various overpotentials, the OCV of an MFC proves a useful parameter. Owing to the various energy losses in MFC, the measured OCV is substantially lower than the thermodynamic value that is estimated theoretically from the difference between the cathode and anode potentials [1]. The difference of the theoretical value and the measured OCV may be described by three aspects: the distribution of two reaction routes of oxygen reduction, the crossover of substrate to the cathode or oxygen to the anode, and the current leakage due to the electron conductivity of the electrolyte [21]. The route for oxygen reduction on the cathode surface is generally described by two- or four-electron transfer reactions. The theoretical potential of oxygen reduction of the two-electron transfer is 0.072 V versus Ag/AgCl at 25 °C, while the four-electron transfer reaction is 0.608 V versus Ag/AgCl at 25 °C [4]. As shown in Fig. 3b, the anode potentials

of the open circuits are similar. However, the cathode potentials of the open circuits for HT and Pt are 229 and 188 mV versus Ag/AgCl, which are higher than those of MW (122 mV v. Ag/AgCl) and CV (117 mV vs. Ag/AgCl). Because this study evaluates the efficiencies of four cathodes using the same synthetic wastewater and mixing conditions, the influence of the concentration loss or substrate crossover on the cathode potentials is seen to be the same. It is possible that the OCVs of the four cathodes are primarily based on the route of oxygen reduction. For the HT and Pt cathodes, it is possible that the fractions of the four-electron transfer reaction of oxygen reduction routes are higher compared to those of the MW and CV cathodes, indicating that the HT and Pt cathodes are more effective for use in the MFCs.

There are some differences between the OCV of the cathodes and the peak voltages of the CVs (Fig. 2). The peak potentials of the four cathodes in the potassium hexacyanoferrate (III) solution may differ from the reduction potentials in air breathable MFC using gas phase oxygen as an electron acceptor. Conducting the CV test using the wastewater as the electrolyte and MFC operating condition may be useful to study the oxygen reduction activity.

Table 2 summarizes the internal cathode resistances were determined using the slope of the linear range of the polarization curve (Fig. 3c). The internal resistance of the MFC with the HT cathode is 48 Ω , which is smaller than that of the Pt (53 Ω). However, the internal resistances are higher for the MW cathode (86 Ω) and the CV cathode (89 Ω). The overpotentials of MFC determining the internal resistance are roughly categorized as follows: (i) activation losses, (ii) bacterial metabolic losses, (iii) mass transport or concentration losses, and (iv) ohmic losses [1]. It is well known that the electric power extractable from organic matter depends on the internal MFC resistance. The high maximum power densities of the HT and the Pt are based on the low internal resistances.

Table 2 OCV, internal resistance, and maximum power density of the MFCs with cathodes prepared using different catalyst loading methods

Cathode	OCV (mV)	R_{in} (Ω)	$P_{d,max}$ (mW m ⁻²)
HT	610	48	833
Pt	570	53	920
CV	499	86	376
MW	506	89	304

R_{in} internal resistance, $P_{d,max}$ maximum power density, HT hydrothermal, Pt platinum, CV cyclic voltammetry, MW microwave

3.3 Internal resistances distribution

The process of obtaining good MFC performance is aided greatly by details on the distribution of internal resistance components and its current dependence. For the real MFC potential, the relationship between the current and the voltage can be described by Eq. (1) [22].

$$V = V_{oc} - (a + b \times \ln I) - I \times R_{ohmic} - c \times \ln \frac{I_L}{I_L - I}, \quad (1)$$

where, V is the voltage, V_{oc} is the open circuit potential, a and b are the activation loss constants, I is the current, R_{ohmic} is the ohmic resistance, c is the concentration loss, and I_L is the limit current. In the above equation ($a+b \times \ln I$), is the activation loss $I \times R_{ohmic}$, is the ohmic loss, and $c \times \ln I_L/(I_L - I)$ is the concentration loss. The total internal resistance (R_i) can be obtained by dividing the sum of the losses by the current as shown in Eq. (2):

$$R_i(\eta_{act} + \eta_{ohmic} + \eta_{conc})/I \quad (2)$$

To describe the internal resistance components according to catalyst loading method, the data for I vs. V from the polarization curve are fitted to Eq. (1) using non-linear regression (Fig. 4). The current immediately before the power overshoot, which frequently occurs in the high current range of MFC, in the I - V curve was used as the limiting current. The I versus V data, for different cathodes fit well in Eq. (1) ($R^2 = 0.98$ for HT, 0.98 for Pt, 0.98 for CV, 0.99 MW). The total internal resistances are 48, 89, 86, and 53 Ω are obtained with the HT, MW, CV, and Pt cathodes from Eq. (2) in the point of maximum power densities obtained. There are similar to the internal resistances calculated from the slope of the linear region of the I - V curve (Fig. 3c). In general, activation energy, the minimum energy required to start a chemical reaction, has a significant influence on the rate of a reaction. On cathode surfaces, activation energy is a kind of potential barrier to be overcome before an oxygen reduction reaction may occur, the rate of which may be increased by lowering that potential barrier using a catalyst [1, 4, 9]. The activation resistance of the oxygen reduction on the cathode is calculated by dividing the potential barrier by the current as $(a+b \times \ln I)/I$. All the activation resistances of the MFCs are seen to decrease as current increases, but vary significantly according to cathode type (Fig. 4a). The activation resistances of the MFCs with the HT and MW cathodes are similar to each other in the current range. However, the MFC with the CV cathode exhibits a slightly lower activation resistance than that of the HT or the MW cathode. The activation resistance of the Pt is the smallest compared to the other cathodes, indicating that Pt is an

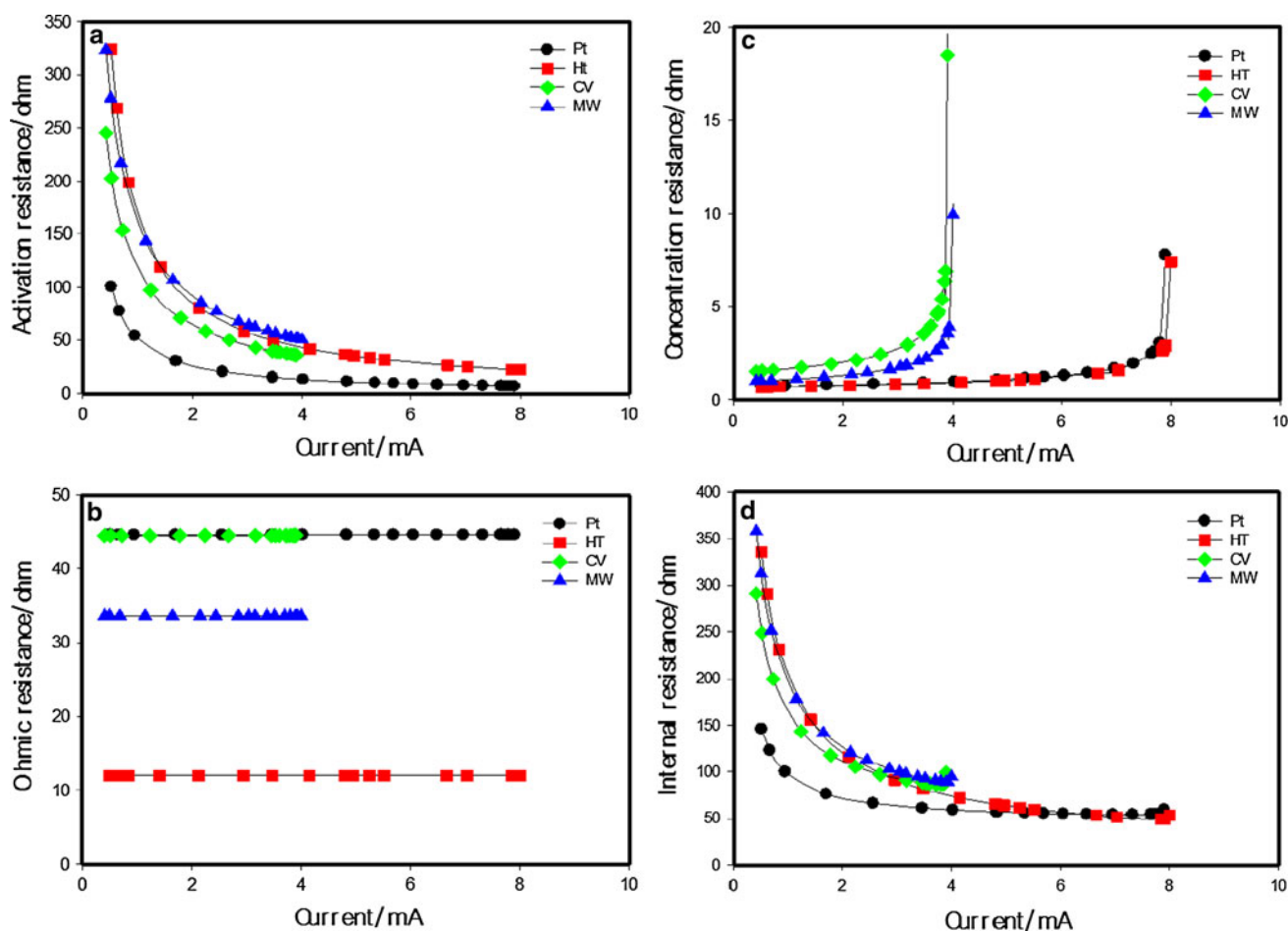


Fig. 4 Internal resistance components of MFCs with cathodes prepared using different catalyst loading methods: **a** ohmic resistance, **b** activation resistance, **c** concentration resistance, and **d** total internal resistances

excellent oxygen reduction catalyst that lowers the potential barrier to activation of the oxygen reduction reaction [1, 5, 9]. In a higher current range, the activation resistance of the MFC with the HT cathode is decreased to a small value that is slightly higher than that of the Pt cathode. This finding indicates that the activation resistance of oxygen reduction is significantly affected by the loading methods of the catalyst on the cathode surface.

Another barrier to be overcome for the oxygen reduction reaction is ohmic resistance of the cathode. This may originate from the primitive electrode conductivity or the catalyst layer of the cathode. In this study, the primitive electrode prepared by the fixing of highly conductive MWCNT on the SUS mesh is highly conductive, but the conductivity of the cathode catalyst layer differs according to the catalyst loading method. The ohmic resistances of the MFCs with the HT and MW cathodes are 12 and 34 Ω , values that are smaller than 43 Ω for the Pt (44.6 Ω). It is possibly that the ohmic resistance of the HT cathode is reduced by the

conductive MWCNT network entangled with the catalyst nanostructure (Fig. 1a) [14]. The ohmic resistances of the CV and Pt cathodes are relatively high compared to those of the HT and MW cathodes. The low conductivity of MnOx contributes to the ohmic resistance of the MFC with the CV cathode [23, 24]. The ohmic resistance of the MFC with the Pt cathode may be reduced through the use of a current collector with high conductivity.

Concentration resistance of the MFC occurs when the mass transport of the cathodic reactants and products (oxygen, proton, electron, and water) limit the current production [1, 5]. In this study, the concentration resistance of the four cathodes gradually increases with increased current and increases rapidly near the limiting current (Fig. 4c). The pattern of the HT concentration resistance with current is similar to that of the Pt, the limiting current of which is measured as approximately about 8 mA. The limiting currents of the MFCs with the MW and CV cathodes are around 4 mA, and the concentration resistance

of the CV cathode is slightly higher than that of the MW cathode over the entire current range. It can be observed that the limiting current is affected by both cathode activation and ohmic resistances. The air side of the three cathodes (HT, MW, and CV) consisted of a hydrophobic MWCNT and PTFE diffusion layer, while the liquid side is a porous nanostructure, indicating that the supply of cathodic reactants (oxygen and proton) and the removal of product (water) results in the same oxygen reduction potentials for the three cathodes. In contrast, the electron supply for the oxygen reduction on the cathode surface may be hindered by the ohmic resistance of the catalyst layer of the cathode, while the electron supply may be restricted by the increased activation resistance in the low current range.

4 Conclusions

MFC performance depends on the oxygen reduction efficiency of the cathode, which is shown here to be significantly affected by the loading method of the catalyst on the cathode surface. By means of the HT method to affix the transient metal catalyst onto the MWCNT support, a conductive MWCNT network entangled with catalyst nanostructure is formed on the catalyst layer of the cathode, reducing the ohmic resistance of the catalyst layer. The maximum power density of the MFC with the HT cathode is 833 mW m^{-2} , which is higher than those of the MW and CV cathodes and slightly lower than that of the Pt cathode. Concentration resistance is dependent on current and increases rapidly near the limiting current. The limiting current results mainly from the electron supply for the oxygen reduction on the cathode surface and is affected by both cathode activation and cathode ohmic resistances.

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